

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT SPECIFICATION

(11) 1 404 291

1 404 291

- (21) Application No. 27049/73 (22) Filed 6 June 1973
 (31) Convention Application No. 60854/72 (32) Filed 16 June 1972 in (19)
 (33) Japan (JA)
 (44) Complete Specification published 28 Aug. 1975
 (51) INT CL² C08L 13/00
 (52) Index at acceptance
 C3P 2H5 2HY D9A7 D9B1A D9B5B D9D2 D9E1 D9E2
 PC13C PC20B PC8B PC8C T2A T2D T2G T2X
 (72) Inventors SHOBU MINATONO and TAKAYUKI OKAMURA



(54) RUBBER COMPOSITIONS

(71) We, KURARAY CO. LTD., a body corporate organised and existing under the laws of Japan, of 1621 Sakazu, Kurashiki-City, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with rubber compositions based on synthetic *cis*-1,4-polyisoprene reinforced with a white filler.

Synthetic *cis*-1,4-polyisoprene rubbers (hereinafter sometimes referred to as "IR") have excellent physical properties like natural rubber but they leave something to be desired on their properties. For example, a vulcanizate of IR incorporating a white filler shows low modulus (stresses at elongation).

Although a pure gum composition of IR differs somewhat in its vulcanization speed in comparison with natural rubbers, there is scant difference in the respective moduli attained (stresses at 300% elongation). However, IR vulcanizates compounded with a white filler show a lower modulus than natural rubbers, so that the former are in general softer than the latter. This softness of IR vulcanizates compounded with a white filler is useful in some applications but a defect in others. Therefore the use of the IR vulcanizate is limited.

In the case of a composition of IR compounded with carbon black, it is possible to improve the modulus of a vulcanizate to an extent equal to that of natural rubbers by such means as increasing the amount of vulcanizing agent, selecting a suitable type of the carbon black or increasing slightly the amount of the carbon black to be mixed with the IR. However, in the case of a composition of IR compounded with a white filler, the modulus of the vulcanizate cannot be improved by the same method as effectively adopted in a composition of IR containing carbon black. For one reason, it is necessary to use considerable amounts of vulcanizing agents and vulcanizing auxiliaries,

inevitably resulting in the marked deterioration of the other desirable physical properties of IR.

It has now been discovered that the modulus of an IR vulcanizate containing a white filler can be notably improved by using IR having bound maleic anhydride or a derivative of it in the molecule in combination with a white filler. In accordance with the present invention, there is provided a reinforced rubber composition comprising a synthetic *cis*-1,4-polyisoprene of a rubber having from 0.01 to 15 molar per cent of bound maleic anhydride or a derivative thereof in the rubber polymer, and a white filler, in which the filler is calcium carbonate, aluminium silicate, silica, magnesium carbonate, calcium magnesium carbonate, magnesium silicate, magnesium oxide, calcium silicate, hard clay, soft clay, calcined clay or a mixture of two or more of them.

The rubber compositions of this invention shown not only a modulus not inferior to that of natural rubbers but also an excellent improvement in mechanical properties, such as tensile strength and tear resistance, and dynamic properties, such as resistance to flex cracking, in comparison with those of ordinary IR.

The modified IR containing the bound maleic anhydride in the polymer can be prepared by reacting maleic anhydride with synthetic *cis*-1,4-polyisoprene. If necessary, a free radical-yielding catalyst or a solvent may be used in this reaction. For example, the reaction can be effected by adding maleic anhydride and a free radical-yielding catalyst to a solution of IR, and heating the resultant homogenous solution under an atmosphere of an inert gas. The reaction in a homogenous solution system may be carried out by using as a solvent aromatic hydrocarbons (e.g. benzene, toluene or xylene) or aliphatic hydrocarbons (e.g. *n*-hexane or *n*-heptane). The reaction can be effected without free radical-yielding catalysts. Alternatively, a solid-state reaction of IR with maleic anhydride can be effected by mixing IR and maleic anhydride

50

55

60

65

70

75

80

85

90

in a milling machine such as roll mill or Banbury type mixer. The production of such a modified IR is described in U.S. patent No. 2,662,874 and U.K. patents Nos. 1,119,629 and 1,204,730.

Maleic anhydride derivatives suitable for use in the modified IR in the present invention include maleic acid, metal salts of maleic acid, maleic acid esters, maleic acid amides and maleic acid imides. The modified IR having bound maleic anhydride derivatives may be produced by various methods. For example, the bound maleic anhydride in IR can be converted into mono ester or di-ester form, amide form or imide form by reacting the IR-maleic anhydride adduct obtained in a manner described above with alcohols such as methanol, ethanol and *n*-butanol or amines such as ammonia, *n*-butyl amine, *i*-butyl amine, allyl amine, di-*n*-butyl amine, mono-ethanol amine, diethanolamine, triethylamine, tri-*i*-propanolamine and pyridine, if necessary, in the presence of a catalyst such as *p*-toluene sulfonic acid. The bound maleic anhydride in IR can be converted into free acid form or acid salt form by hydrolysing the acid anhydride group using acid or alkali. Alternatively, modified IR having bound maleic anhydride derivatives may be produced by, for example, reacting IR with maleic acid esters, maleic acid amides or maleimides.

A modified IR containing in the molecule both maleic anhydride and one or more of its derivatives may be used. A mixture of a modified IR containing maleic anhydride and a modified IR containing a derivative of maleic anhydride may also be used. The word "maleic anhydride" is hereinafter used to include the maleic anhydride derivative.

The amount of maleic anhydride introduced into the IR, i.e. the bound maleic anhydride content, may be determined appropriately, according to the desired modulus of the vulcanizate, within the range 0.01 to 15 mol per 100 recurring units of isoprene monomer in the IR polymer. When the bound maleic anhydride content is less than 0.01 molar percent, the desired effect cannot be achieved. When the content is more than 15 molar percent, the processability and other physical properties of the resulting modified IR lower markedly. A modified IR containing 0.03 to 5 mol of maleic anhydride introduced per 100 units of isoprene monomer in the IR polymer is preferred for obtaining a composition showing a modulus equal to that of natural rubbers while keeping the excellent processability and physical properties of IR. A modified IR having a small gel content and containing 0.03 to 0.9 mol of the bound maleic anhydride per 100 units of isoprene monomer in the IR polymer is particularly suitable in the present invention. In the reaction for introducing maleic anhydride into IR, gelation generally takes place to give a modified IR having a

higher gel content than that of the starting IR. The workability on roll of a modified IR having a high gel content is inferior, and this poor workability also lowers the physical properties of the product. A modified IR having a high gel content shows shrinkage during the calendering operation. So, it is most desirable in this invention to use a modified IR with substantially no increase of gel content as compared with the starting IR, and having the bound maleic anhydride content of 0.03 to 0.9 mol per 100 recurring units of isoprene monomer. Because the rubber compositions containing a white filler prepared by using such a modified IR is the most excellent in total evaluation on modulus, processability and other physical properties. Such a modified IR containing 0.03 to 0.9 mol of maleic anhydride per 100 recurring units of isoprene monomer and having substantially no increased gel content may be advantageously prepared by carrying out the reaction in an inert solvent under an atmosphere of an inert gas at a temperature of 0—150°C using maleic anhydride and a free-radical-yielding catalyst under the following conditions: (A) the amount of maleic anhydride is in the range of 0.04 to 3 part by weight per 100 parts by weight of high *cis*-1,4-polyisoprene rubber. (B) the value obtained from multiplication of [the amount of the free-radical-yielding catalyst expressed by millimol per 100 g of said rubber] × [catalyst efficiency] is in the range of 0.016 to 1.03, and (C) the value of (A)/(B) is in the range of 0.24 to 24.2.

The term "gel" in this invention denotes a benzene-insoluble portion that can be filtered with a glass filter having a pore diameter of 20 to 30 μ .

The term "synthetic *cis*-1,4-polyisoprene rubber" in the present specification means a polymer having a *cis*-1,4 content of at least 80% which can be prepared by polymerizing isoprene in the presence of a Ziegler catalyst or anionic catalyst. If evaluated on the whole physical properties, it is preferable to use IR having a *cis*-1,4 content of at least 95%.

More specific examples of the white filler used in this invention are precipitated calcium carbonate, ultra-fine activated calcium carbonate, hard clay, soft clay, calcined clay, hydrated silica and anhydrous silica. The white filler may be used in admixture with a small amount of carbon black. The white filler may be used in an amount in the range of 5 to 250 parts by weight, favorably 20 to 150 parts by weight per 100 parts by weight of the modified IR having bound maleic anhydride. In addition to the white filler, other conventional compounding ingredients for rubbers such as vulcanizing agents, vulcanization accelerators, zinc oxide, stearic acid, extender oils and antioxidants may of course be added to obtain the desirable vulcanizates.

The modified IR having bound maleic anhydride may be used singly or in combination with other rubbers such as conventional IR, polybutadiene rubbers, styrene-butadiene copolymer rubbers and ethylene-propylene copolymer rubbers in the rubber composition of this invention. Vulcanization may be effected with heat in the presence of vulcanizing agents such as sulfur, sulfur compounds and peroxides, and vulcanization accelerators.

The present invention is illustrated in the following examples.

Example 1.

Cis-1,4-polyisoprene rubber having *cis*-1,4 content of 98%, an intrinsic viscosity of 3.7 dl/g measured at 30°C in toluene and a gel content of 2%, was prepared by polymerizing isoprene with a Ziegler type catalyst. Said rubber is hereinafter referred to as "IR(A)".

To a solution of IR(A) (210 g) in xylene (7 lit.), maleic anhydride (hereinafter referred to as "MAn") and benzoyl peroxide (hereinafter referred to as "BPO") each in

a prescribed amount were added according to Sample Nos. A to F of Table 1 below, and the resultant mixture was stirred at 100°C for 3 hours in a nitrogen atmosphere. The reaction mixture was poured in to a large amount of acetone, and the precipitated polymer was dried to give maleic anhydride-IR(A) adducts (Samples A to F in Table 1). No production of a gel was observed in Samples A to D but gel contents of 21% and 53% were observed respectively in Samples E and F.

Using Samples A to F, starting IR(A) and natural rubber, compositions containing precipitated calcium carbonate were prepared by a 6-inch roll mill according to the compounding recipe shown in Table 2 below. As is clearly shown in Table 1, the precipitated calcium carbonate composition of IR(A) having the bound maleic anhydride showed a marked improvement in the modulus (M 300) in comparison with that of the starting IR(A), even with the content of maleic anhydride of only about 0.1 mole per 100 units of isoprene monomer.

TABLE 1

Sample No.	Amount of BPO in % by weight for the rubber	Amount of MAn (phr)	Bound MAn content*	M300** (kg/cm ²)
A	0.004	0.04	0.02	27
B	0.1	0.45	0.09	35
C	0.05	0.65	0.21	40
D	0.15	1.2	0.41	43
E	0.08	9	0.82	56
F	0.11	12	1.25	70
IR(A)	—	—	—	22
Natural rubber	—	—	—	40

Note: *) Measured by titrating a solution of the sample in benzene with a solution of sodium hydroxide in methanol/benzene mixture. Mol number of MAn bound per 100 units of isoprene monomer.

**) Stresses at 300% elongation (vulcanized at 145°C for 30 minutes), 25°C, tension speed 50 cm/min.

TABLE 2

Rubber	100 parts by weight
Precipitated calcium carbonate	75 "
Zinc oxide	5 "
Stearic acid	3 "
Accelerator DM 1)	1 "
Accelerator DT 2)	0.3 "
Sulfur	3 "
Antioxidant NS-6 3)	1 "

Note: 1) Dibenzothiazyl disulfide.

2) Diorthotolyl guanidine.

3) 2,2'-Methylenebis(4-methyl-6-tert-butylphenol).

5 The detailed physical properties of the vulcanizates prepared from Sample D and the starting IR(A) are shown in the Table 3 below. As recognized from the table, Sample D (IR(A) having the bound maleic an-

hydride) has not only increased modulus but also increased tensile strength, tear resistance and resistance to flex cracking in comparison with the starting IR(A).

10

TABLE 3

	Vulcanization time (min) (145°C)	Sample D	IR(A)
Stress at 300% elongation (kg/cm ²)	20	41	21
	30	43	22
Tensile strength (kg/cm ²)	20	249	190
	30	256	196
Elongation (%)	20	670	700
	30	680	710
Tear resistance (kg/cm)	20	40	25
	30	39	24
Hardness (JIS A)	20	53	51
	30	54	52
Resistance to flex-cracking by DeMattia tester (Flex number required for growing from 2 mm to 8mm) (ASTM D 430-59 Method B and ASTM D 813-59)	20	2.5×10 ⁴	0.9×10 ⁴
	30	2.2×10 ⁴	0.8×10 ⁴

Physical properties were measured according to the Rule of JIS K 6301.

Example 2.

15 Using Sample B, Sample D, IR(A) and

the natural rubber used in Example 1, vulcanizates containing hydrated silica were prepared using the ingredients described in Table 4.

TABLE 4

Rubber	100 parts by weight
Hydrated silica	45 „
Zinc oxide	5 „
Stearic acid	3 „
DHA ¹⁾	3 „
Accelerator DM	1 „
Accelerator D ²⁾	0.3 „
Sulfur	2 „
Antioxidant NS-6	1 „

Note: 1) Dicyclohexylamine.

2) Diphenylguanidine.

Vulcanizing condition: 145°C, 25 minutes.

Physical properties of the vulcanizates obtained were measured. It was clear in Table 5 that the hydrated silica composition of

Sample B and Sample D showed a marked improvement on M 300 and some improvement in the tensile strength.

TABLE 5

Sample No.	M 300 (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation at break (%)
B	53	280	610
D	100	292	500
IR(A)	29	270	650
Natural rubber	50	278	620

Example 3.

10 Using Sample B, Sample C, IR(A), a blend of equal weights of Sample C and

IR(A), and natural rubber, vulcanizates containing Dixie clay were prepared using the ingredients shown in Table 6.

TABLE 6

Rubber	100 parts by weight
Dixie clay	75 "
Zinc oxide	5 "
Stearic acid	3 "
D H A	1 "
Accelerator DM	1 "
Accelerator D	0.3 "
Sulfur	2 "
Antioxidant NS-6	1 "

Note: Vulcanizing condition: 145°C, 25 minutes.

The M300 of the obtained vulcanizate was measured. As shown in Table 7, the composi-

tion of this invention showed a markedly excellent result.

5

TABLE 7

Sample No.	M300 (kg./cm ²)
B	93
C	124
C+IR(A) Blend in same amount IR(A)	81 40
Natural rubber	110

Example 4.

Cis-1,4-polyisoprene rubber having cis-1,4 content of 98% and an intrinsic viscosities of 4.2 dl/g measured at 30°C in toluene, which was prepared by polymerizing isoprene with a Ziegler type catalyst. Said rubber is hereinafter referred to as "IR(B)".

IR(B) (1 kg) and maleic anhydride (1.0 phr or 2.5 phr) were milled using a small scale Banbury mixer. Operating conditions of the mixer were as follows: rotational speed of 115 r.p.m.; initial temperature of 75°C; and milling time of 7 minutes. The thus obtained IR(B)-maleic anhydride adduct

(of which adduct obtained by reacting 1.0 phr of maleic anhydride with IR(B) was designated Sample G and had a bound maleic anhydride content of 0.47 mole percent and the adduct obtained by reacting 2.5 phr of maleic anhydride with IR(B) was designated Sample H and had a bound maleic anhydride content of 1.28 mole percent) was compounded by a conventional 8-inch roll mill according to the composition of Table 8 and vulcanized at 145°C for 35 minutes.

As shown in Table 9, the physical properties of the vulcanizate were greatly improved.

25

30

TABLE 8

Rubber	100 parts by weight	
Precipitated calcium carbonate	75	„
Zinc oxide	5	„
Stearic acid	3	„
DHA	1	„
Accelerator MSA ¹⁾	1	„
Sulfur	2	„
Antioxidant MS-6	1	„

Note: 1) N-(benzothiazol-2-ylthio)morpholine.

TABLE 9

Sample No.	Amount of MAn added initially (phr)	M300 (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation at break (%)
G	1.0	52	190	470
H	2.5	100	183	510
IR(B)	—	25	172	700

Example 5.

To a solution of Sample D (150 g; used in Example 1) in benzene (5 lit.), methanol (0.8 lit.) was added and the mixture was refluxed for 3 hours in a nitrogen atmosphere to esterify the bound maleic anhydride in IR(A). The reaction mixture was poured into a large amount of methanol to precipitate the polymer, which was dried to give Sample J.

In another procedure, 10% hydrochloric acid (10 ml) was added to a solution of Sample D (150 g) in benzene (5 lit.), and then the resultant mixture was refluxed with stirring for 3 hours to hydrolyse the bound maleic anhydride. The reaction mixture was poured into a large amount of methanol to precipitate the polymer, which was dried to give Sample K.

The compositions were prepared using said two samples according to Table 2 and vulcanized at 145°C for 45 minutes. Sample J showed a M300 of 41 kg/cm², and Sample K showed a M300 of 50 kg/cm², whereby a marked improvement on the modulus was achieved in comparison with that of the starting IR(A).

WHAT WE CLAIM IS:

1. A reinforced rubber composition comprising a synthetic *cis*-1,4-polyisoprene rubber as herein defined having 0.01 to 15 molar per cent of bound maleic anhydride or a derivative thereof in the rubber polymer, and a white filler, in which the filler is calcium carbonate, aluminium silicate, silica, magnesium carbonate, calcium magnesium carbonate, magnesium silicate, magnesium oxide, calcium silicate, hard clay, soft clay, calcined clay, or a mixture of two or more of them.

2. A composition as claimed in Claim 1, in which from 5 to 250 parts by weight of the white filler is present per 100 parts by weight of the rubber plus maleic anhydride or derivative thereof.

3. A composition as claimed in Claim 2, in which from 20 to 150 parts by weight of the white filler is present per 100 parts by weight of the rubber plus maleic anhydride or derivative thereof.

4. A composition as claimed in Claim 3 that has been vulcanized.

5. A composition as claimed in any preceding claim, in which the white filler is calcium

carbonate, aluminium silicate and/or silica.

- 5 6. A composition as claimed in any preceding claim, in which from 0.03 to 0.9 mol of the bound maleic anhydride or derivative thereof is present per 100 recurring units of isoprene monomer in the polyisoprene.

7. A composition as claimed in any preceding claim, in which the derivative of maleic anhydride is maleic acid, a maleic acid ester,

a maleic acid amide or a maleic acid imide.

8. A composition as claimed in claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

10

For the Applicants,
D. YOUNG & CO.,
Chartered Patent Agents,
9 & 10 Staple Inn,
London WC1V 7RD.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.